HICKORY SMOKE

Composition of Hickory Sawdust Smoke. Furans and Phenols

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Eighteen components derived from hickory wood smoke have been separated by gas-liquid chromatography and identified by comparing the retention times and infrared spectra with known authentic samples. Three additional components have been given tentative identifications and three remain unidentified. Five components of wood smoke—acetol, 2-cyclopentenone, cyclotene, 4-vinylguaiacol, and eugenol—have not been reported, previously.

Food products have been processed for countless years by exposure to wood smoke. This treatment contributes to desirable flavor and color and exerts a preservative effect. With the development of other methods of preservation, foods now are smoked mainly for their sensory qualities. In recent years, beginning with the work of Pettet and Lane in 1940 (*10*), intensive studies have been made on the parameters of formation and the composition of smoke for the purpose of improvement in the quality of smoked meat and food products. Phenols have been reported primarily responsible for the smoky aroma and taste of food products (*7, 17*) although other major classes—such as acids and carbonyls—have been identified in smoke (*4, 5, 12, 16*).

Early investigations of the phenolic fraction of smoke preparations reported determination of phenols on the basis of total phenols, using colorimetric methods with phenol or guaiacol as standards. However, this technique has two deficiencies: The color values for the various phenols are not always equivalent, so true quantitation was never achieved (*13, 18*); and individual phenols were not identified. In recent years, a number of studies have been carried out in which phenolic components of wood smoke have been identified. However, the methods of generating the smoke, collecting the phenolic fraction, and identifying the components have not been uniform or reproducible. Correlation of the results from these investigations to obtain meaningful information about the desirable phenol composition of smoke and the best parameters for its production is difficult.

Goos (*2*) has tabulated references to more than 200 compounds that were found in the condensate of the destructive distillation of wood. However, the combustion of wood for the smoking of food items involves both the destructive distillation process and oxidative interactions of the products of this process. As a result, the composition of wood smoke could be different from that of the condensate. While most of the components of smoke reported to date were found also in the destructive distillation condensates, independent identifications must be made of components of all smoke preparations to confirm their absence or presence under varying conditions of smoke production and treatment.

Eight literature reports have been collected in which individual phenols were identified (*1, 3, 6, 8–10, 15, 19*). Of approximately 30 phenols identified, many have not been reported by more than one investigator. The method used for identification was important with respect to the number of phenols identified. Only limited numbers were detected and identified by paper chromatography. The sensitivity of paper chromatographic methods is such that many components present in wood smoke may not be detected. Furthermore, identifications based solely on the comparison of GLC or paper chromatography retention times, in which a number of different compounds can give the same retention values, leave some doubt as to the actual presence of some of these compounds in smoke. In recent reports, however, in which GLC techniques were used, Jahnsen (*8*) identified 12 phenols and Sikorski (*14*) reported 17 peaks that had phenolic characteristics as determined by functional group analysis. Unfortunately, Sikorski did not identify a single one of his components.

Since studies of meat processing are likely to require a knowledge of smoke composition and reactions, this laboratory is involved in the development of reproducible methods of smoke generation which can be used to study the effects of variables, such as combustion temperature, air flow, sawdust source, and others on the chemical composition of smoke. The data reported in this paper present information on the composition of a fraction of wood smoke consisting primarily of phenols; the results of investigations of other components of this smoke preparation are being studied.

Experimental

The smoke used in this work was generated in a laboratory scale apparatus (Figure 1) in which various parameters of smoke generation could be controlled. This smoke generator was constructed from two glass cylinders consisting of an inner tube, 9 inches long by $1^7/_8$ inches in diameter, wrapped with a Nichrome wire heating element and an outer tube, $8^1/_8$ inches long by $2^1/_4$ inches in diameter. The glass heater was fitted with stainless steel ends. The sawdust charge was contained in a stainless steel, wire mesh trough placed on the bottom of the horizontally fixed generator. Three thermocouples were fitted into the apparatus to measure the temperatures within the sawdust bed and of the smoke at the exit port. Five-gram quantities of hickory sawdust having a moisture content of 7% were placed in the smoke generator and air was passed through at a constant flow rate of 500 ml. per minute. The average temperature in the center of the sawdust bed during smoke generation was 450° C.

Smoke preparations were obtained by two procedures: (1) A concentrated phenolic fraction was prepared by bubbling smoke through a trap containing 1*N* sodium hydroxide, acidifying the alkaline solution in the cold to pH 6.0, extracting with chloroform, and concentrating by evaporating the solvent with nitrogen; (2) whole smoke condensate was collected by passing the smoke through dry ice–acetone traps.

The smoke preparations were subjected to gas-liquid chromatography. Components of smoke preparations were separated with a Perkin-Elmer Model 800 dual-column gas chromatograph fitted with a flame ionization detector and equipped with a 4 to 1 ratio stream splitter to permit collection of the peaks as they emerged. Two stainless steel columns, 6 feet by $^1/_8$-inch o.d., packed with 15% Carbowax 20M–terephthalic acid on 60- to 80-mesh Gas Chrom P, were used. The operating conditions were: temperature programming from 70° to 170° C. at 5° per minute with helium carrier gas at a flow of 125 cc. per minute. Injection port and detector temperatures were 210° and 200° C., respectively.

To obtain sufficient material to identify some of the minor components, rough, preparatory separation procedures were carried out prior to the final separation and isolation with the P-E Model 800. For the preparative work, a Wilkens Aerograph A-700 gas chromatograph, equipped with a thermal conductivity detector and containing a 12-foot by $^1/_4$-inch o.d. stainless steel column, packed with 30% Carbowax 20M–terephthalic acid on 60- to 80-mesh Gas Chrom P, was used. The column was operated at a temperature program of 70° to 170° C. and helium flow of 125 cc. per minute. Injection port and detector temperatures were 175° and 200° C., respectively.

Preliminary identification of the various components was made by comparing the retention times with those of known compounds. Smelling the components as they emerged from the exit port of the chromatograph also afforded, in many cases, a very sensitive and rapid lead toward component identification. The individual components were trapped in a capillary tube. The tube was rinsed with approximately 6 μl. of carbon tetrachloride and the solution transferred to a 0.1-mm. path length KBr type D microcavity cell obtained from the Barnes Engineering Co., Stamford, Conn. The infrared spectra were obtained in a Perkin-Elmer Model 421 spectrophotometer fitted with a beam condenser. The spectra of the trapped materials were compared with those of authentic standard samples.

The hickory sawdust employed in this work was obtained as such from Koch Supplies Inc. and is the same as used in commercial smoke generators. Reagent grade standard samples of chemicals used for the identification of smoke components were purchased from commercial sources, with the following exceptions. Samples of 4-propylguaiacol and 2,6-dimethoxy-4-propylphenol were obtained through the courtesy of the Institute of Paper Chemistry, Appleton, Wis. The 2,6-dimethoxy-4-methylphenol and 2,6-dimethoxy-4-ethylphenol were obtained through the courtesy of Cliffs Dow Chemical Co., Marquette, Mich. An authentic sample of 4-vinylguaiacol was prepared from the thermal decomposition of ferulic acid by the procedure of Phillips and Goss (*77*) and its identity confirmed by infrared and mass spectra.

Results and Discussion

Figure 2 is a representative chromatogram of the components of hickory smoke collected in the 1*N* sodium hydroxide trap. The identities of the various peaks are listed in Table I. Positive identification is indicated only when both GLC elution time and infrared spectra agree with those of the authentic standard material. Tentatively identified components, however, are shown also. This smoke concentrate consists primarily of phenolic and furan derivatives. The major components, based on peak area, are furfuryl alcohol, guaiacol, 4-methylguaiacol, 2,6-dimethoxyphenol, and 2,6-dimethoxy-4-methylphenol. Of the minor components, peak 16 was tentatively identified as eugenol (4-allylguaiacol) on the basis of GLC retention time, and the infrared spectrum in which the O-H stretching vibration is located at 3560 $cm.^{-1}$, similar to that of the other methoxy substituted phenols reported in this article. The over-all infrared spectrum contains all of the

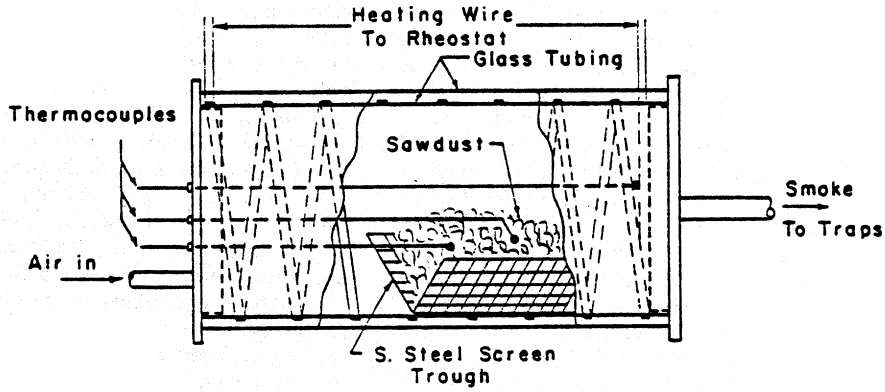

Figure 1. Smoke generator for the production of hickory sawdust smoke

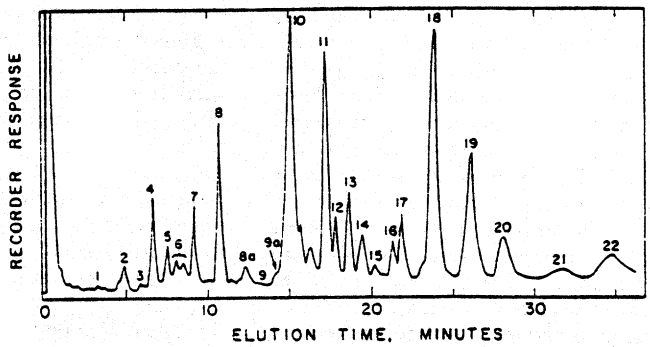

Figure 2. Gas chromatogram of smoke components trapped in 1*N* NaOH

Table I. Components of Smoke Preparations

Peak No.[a]	Identity	Retention Time, Min. Found	Retention Time, Min. Standard	Method Confirmed
1	Acetol (1-hydroxypropanone)	3.3	3.1	GLC, IR
2	2-Cyclopentenone	4.7	4.4	GLC, IR
3	Acetic acid	5.6	5.5	GLC, IR, odor
4	Furfural	6.8	6.6	GLC, IR, odor
5	Unidentified (nonaromatic aldehyde)	7.7		
6	Unidentified	8.0		
7	5-Methylfurfural	9.4	9.4	GLC, IR
8	Furfuryl alcohol	11.0	11.0	GLC, IR
8a	Unidentified	12.5		
9	Veratrol (1,2-dimethoxybenzene)	13.1	13.3	GLC
9a	Cyclotene (3-methylcyclopent-2-en-2-ol-1-one)	14.4	14.8	GLC, IR
10	Guaiacol (2-methoxyphenol)	15.2	15.5	GLC, IR, odor
11	4-Methylguaiacol	17.3	17.4	GLC, IR
12	Phenol	17.9	18.2	GLC, IR
13	4-Ethylguaiacol	18.7	18.8	GLC, IR
14	*m*-Cresol	19.5	19.8	GLC
15	4-Propylguaiacol	20.3	20.7	GLC, IR
16	Eugenol (4-allylguaiacol)	21.4	21.7	GLC
17	4-Vinylguaiacol	21.9	21.7	GLC, IR
18	2,6-Dimethoxyphenol	23.9	23.5	GLC, IR
19	2,6-Dimethoxy-4-methylphenol	26.2	26.7	GLC, IR
20	2,6-Dimethoxy-4-ethylphenol	28.0	28.4	GLC, IR
21	2,6-Dimethoxy-4-propylphenol	31.6	32.2	GLC, IR
22	Vanillin	34.8	35.0	GLC, IR, odor

[a] The peak numbers correspond to the peaks in Figures 2 and 3.

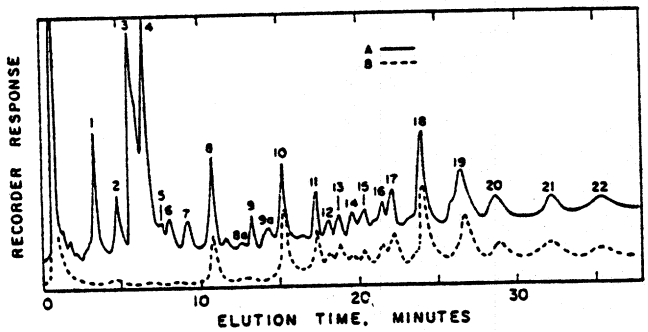

Figure 3. Gas chromatogram of components of cold-trapped smoke condensate

Curve A, Whole condensate. Curve B, sodium hydroxide extract of condensate

strong and medium bands identical to the authentic sample of eugenol, with the exception of a few additional weak bands in the C-H region between 2900 and 2980 cm.$^{-1}$ and an additional weak band at 1700 cm.$^{-1}$. These extra bands may be due to bleeding of the substrate used in the GLC column or other impurity. Peak 14 has the same retention time as *m*-cresol, and its infrared spectrum, in which the O-H stretching vibration is located at 3610 cm.$^{-1}$, is characteristic of alkyl-substituted phenols. The locations of other bands are similar to, but not exactly like, those of authentic *m*-cresol. Other investigators (*7, 8, 9, 19*) have cited the presence of *o*-, *m*-, and *p*-cresols in substantial amounts, whereas the authors found little or none of these compounds present under their conditions of smoke generation. Peak 9 was tentatively identified as veratrol on the basis of having the same GLC retention time as the authentic sample.

Acetol, 2-cyclopentenone, cyclotene, 4-vinylguaiacol and the tentatively identified eugenol listed in Table I have not been identified previously in wood smoke.

The process of trapping smoke in sodium hydroxide may result in errors in the composition of the fraction due to reactions that can occur in alkaline solution. To avoid such possible changes, whole smoke condensate was prepared by trapping in the cold. Figure 3*A* is a representative chromatogram of this condensate. Furfural and acetic acid are by far the most predominant constituents. The other major peaks are acetol, furfuryl alcohol, guaiacol, 4-methylguaiacol, 2,6-dimethoxyphenol, and 2,6 - dimethoxy - 4 - methylphenol. Comparison of the key peaks of Figures 2 and 3*A* by retention times and infrared spectra substantiated the identity of similarly numbered peaks in both chromatograms. As a further confirmatory procedure in the identification of the phenolic constituents, a chloroform solution of the smoke condensate was extracted with 1*N* sodium hydroxide, which in turn was acidified to pH 6.0, then re-extracted with chloroform. Figure 3*B* represents the phenolic fraction of the smoke condensate thus obtained. Comparison of Figure 3,*B* with Figure 2 reveals the similarity of the two preparations in the area of the phenolic components. The alkaline extraction of the whole smoke solution, however, removed fewer nonphenolic compounds than the original procedure of bubbling the entire smoke through the alkaline solution.

In the study reported here, 11 phenols have been identified unambiguously, and 3 phenols have been tentatively identified. Although there are a greater number of peaks in the chromatogram of the phenolic fraction, a few of these peaks have not been identified because they are present in too low a concentration to be readily isolated. However, the fact that they are present in such low concentrations does not necessarily mean they are unimportant in the over-all flavor pattern of the phenolic fraction. Possibly, these compounds may modify the aroma of those present in larger concentrations, or they may have an extemely low odor threshold concentration and actually be responsible for a major part of the wood smoke aroma. The necessity may arise for isolation and identification of these minor constituents.

Preliminary investigations have shown that the essential smoke odor is retained by the whole smoke condensate even when all the material eluting before furfuryl alcohol and after 2,6-dimethoxy-4-propylphenol has been removed. These results are in agreement with those of other authors (*7, 9, 17*) that the phenolic compounds are of major importance in smoke flavor.

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